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(Reaffirmed 1998)

Indian Standard

METHOD FOR COLORIMETRIC DETERMINATION OF TUNGSTEN

UDC 543·432 : 546·78

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BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

Gr 2

October 1989

Indian Standard

METHOD FOR COLORIMETRIC DETERMINATION OF TUNGSTEN

0. FOREWORD

0.1 This Indian Standard was adopted by the Bureau of Indian Standards on 15 December 1988, after the draft finalized by the Chemical Standards Sectional Committee had been approved by the Chemical Division Council.

0.2 Tungsten in the concentration range of 10-500 ppm in different materials may be determined colorimetrically by any of the following methods:

a) Thiocyanate with a reducing agent;
b) Toluene-3, 4-dithiol;
c) Hydroquinone; and
d) Rhodamine B.

0.2.1 The first two methods are of importance because of their accuracy while the other two are useful for rough estimation of tungsten.

0.3 This standard, however, does not cover colorimetric method using hydroquinone and Rhodamine B.

0.4 Molybdenum reacts similarly as tungsten with these regents and has to be separated before tungsten is determined.

0.4.1 This separation may be done by precipitation of molybdenum as orthophosphate or sulphide or by extraction of its complex with an organic solvent depending on the relative amounts present in the material.

0.5 In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960*.

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*Rules for rounding off numerical value (*revised*).

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1. SCOPE

1.1 This standard prescribes two colorimetric methods for determination of tungsten using (a) thiocyanate with a reducing agent; and (b) toluene-3, 4-dithiol.

2. QUALITY OF REAGENTS

2.1 Unless specified otherwise, pure chemicals and distilled water (*see* IS : 1070-1977*) shall be used in tests.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the result of analysis.

3. PREPARATION OF TUNGSTEN SOLUTION FROM SAMPLES

3.1 Metals and Alloys

3.1.1 *Iron and Steel* — containing about 5 percent tungsten.

3.1.1.1 *Reagents*

a) *Concentrated hydrochloric acid* — *See* IS : 265-1976†.
b) *Concentrated nitric acid* — *See* IS : 264-1976‡.
c) *Perchloric acid* — 60 percent.
d) *Dilute hydrochloric acid* — (1 : 1).
e) *Dilute hydrochloric acid* — (1 : 20).
f) *Concentrated sulphuric acid* — *See* IS : 266-1977*.
g) *Hydrofluoric acid* — *See* IS : 10332-1982†.

3.1.1.2 *Procedure* — Treat 1 g sample with 30 ml concentrated hydrochloric acid, cover and heat. Add 10 ml of concentrated nitric acid and digest near the boiling point until the precipitate is pure yellow. Cool slightly and add 30 ml of perchloric acid and heat to white fumes with the cover raised. To the residue, add 30 ml 1 : 1 hydrochloric acid and boil for 15 minutes. Wash the cover glass and the sides of the beaker with hot water. Add some paper pulp, digest on a steam bath at 80°C for 45 minutes.

Filter and wash the precipitate with 8 portions of 1 : 20 hydrochloric acid. Ignite the residue with paper in a platinum crucible. Add 2 ml of hydrofluoric acid to the cooled ash and 2 drops of concentrated sulphuric acid and heat to fumes and drive off all the residual acid. Fuse the residue with 5 g of mixed sodium and potassium carbonates. Extract the fused melt with water.

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*Specification for water for general laboratory use (*second revision*).

†Specification for hydrochloric acid (*second revision*).

‡Specification for nitric acid (*second revision*).

*Specification for sulphuric acid (*second revision*).

†Specification for hydrofluoric acid, aqueous.

Transfer to a 100 ml volumetric flask and make up to the volume. Use aliquots (*see* **4.3**).

3.1.2 *Iron and Steel* — (with low tungsten content).

3.1.2.1 *Reagents*

a) *Acid mixture* — 1 000 ml of this mixture shall contain 150 ml of concentrated sulphuric acid (*see* IS : 266-1977*) and 150 ml of 85 percent orthophosphoric acid.

b) *Concentrated hydrochloric acid* — *See* IS : 265-1976†.

c) *Concentrated nitric acid* — *See* IS : 264-1976‡.

3.1.2.2 *Procedure* — Treat 0·5 g sample with 30 ml of acid mixture and 10 ml of concentrated hydrochloric acid in a glass beaker. After complete dissolution, add 5 ml of concentrated nitric acid and evaporate to sulphur trioxide fumes. Cool, dilute to 100 ml and take aliquots (*see* **4.3**).

3.1.3 *Zirconium Alloys*

3.1.3.1 *Reagents*

a) *Cocentrated nitric acid* — *See* IS : 264-1976‡.

b) *Hydrofluoric acid* — *See* IS : 10332-1982§.

c) *Concentrated sulphuric acid* — *See* IS : 266-1977*.

3.1.3.2 *Procedure* — Transfer 0·25 to 0·5 g of sample in 150 ml beaker mode of polytetrafluoro-ethylene (PTFE) of equivalent resistant material. Add sufficient water to cover the sample. Add 6 drops each of concentrated nitric acid and hydrofluoric acid, and 5 ml of concentrated sulphuric acid. Heat gently to dissolve and evaporate to dense fumes. Cool, dilute and make up to a known volume and use aliquots (*see* **4.3**).

3.1.4 *Titanium Alloys*

3.1.4.1 *Reagents*

a) *Dilute sulphuric acid* — 1 : 3 (*v/v*).

b) *Dilute hydrofluoric acid* — *See* IS : 10332-1982§.

c) *Hydrogen peroxide solution* — 30 percent.

3.1.4.2 *Procedure* — Transfer 0·1 to 0·2 g of sample to a 150 ml PTFE beaker or equivalent resistant material. Add 20 ml of 1 : 3 sulphuric acid and 2 to 3 drops of hydrofluoric acid. Heat gently until the sample is dissolved. Add 30 percent hydrogen peroxide dropwise until the purple colour of reduced titanium is discharged and a permanent yellow colour of peroxidized titanium is formed. Evaporate to fumes and cool. Make up to 100 ml and take aliquots (*see* **4.3**).

3.2 Ores

3.2.1 *Ores Containing Molybdenum and Arsenic*

3.2.1.1 *Reagents*

a) *Dilute orthophosphoric acid* — 1 : 3 (*v/v*).

b) *Concentrated hydrochloric acid* — *See* IS : 265-1976*.

c) *Dilute hydrochloric acid* — 1 : 4 (*v/v*).

3.2.1.2 *Procedure* — To 1 g of finely ground sample, add 1 ml of 1 : 3 orthophosphoric acid and 40 ml of concentrated hydrochloric acid. Digest on a steam bath for 20 minutes and evaporate to dryness. Cool and add 10 ml of 1 : 4 hydrochloric acid, and digest for 15 minutes. Cool and dilute to 50 ml. Filter into 100 ml volumetric flask, make up to volume and use aliquots (*see* **4.3**).

3.2.2 *Sulphide Ores*

3.2.2.1 *Reagents*

a) *Sodium hydroxide* — *See* IS : 376-1986†.

3.2.2.2 *Procedure* — Ignite 0·5 g sample in an iron crucible at 850°C until the sulphur has been completely driven off as oxides. Fuse the cooled residue with 2 g of sodium hydroxide. Take up with 50 ml of water and filter into a 100-ml volumetric flask. Dilute to volume and take aliquot (*see* **4.3**).

3.2.3 *Silicate Rocks* — Two methods given below can be used for the preparation of solution. However, fusion with sodium carbonate or sodium peroxide, or sodium or potassium pyrosulphate shall be avoided, if possible, since alkali salt prevents complete extraction of tungsten by acid digestion of the melt.

3.2.3.1 *Reagents*

a) *Dilute sulphuric acid* = 6 N.

b) *Dilute sulphuric acid* — 5 percent.

c) *Concentrated nitric acid* — *See* IS : 264-1976‡.

d) *Dilute hydrofluoric acid* — *See* IS : 10332-1982§.

e) *Potassium pyrosulphate*

f) *Tartaric acid* — 5 percent.

3.2.3.2 *Method A* — Transfer 1 g of finely ground material to a platinum dish and add 5 ml of 6 N sulphuric acid, 2 ml of concentrated nitric acid and 5 ml of hydrofluoric acid. Evaporate to dryness and heat the residue until

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*Specification for sulphuric acid (*second revision*).

†Specification for hydrochloric acid (*second revision*).

‡Specification for nitric acid (*second revision*).

§Specification for hydrofluoric acid, aqueous.

*Specification for hydrochloric acid (*second revision*).

†Specification for sodium hydroxide A.R. (*third revision*).

‡Specification for nitric acid (*second revision*).

§Specification for hydrofluoric acid, aqueous.

fumes of sulphuric acid cease to come off. Add 1 ml of 6 N sulphuric acid and a few millilitres of water to the dish, warm and stir to dissolve salts. Evaporate to dryness and fume off the excess of sulphuric acid at 350°C. Add 1 ml of 6 N sulphuric acid and 10 ml of water and digest slowly below the boiling point for 15 minutes while stirring at intervals. Filter and make up volume in a 100-ml volumetric flask and take aliquots (*see* **4.3**).

3.2.3.3 *Method B* — Fuse 1 g of finely powdered ore with 5 g of potassium pyrosulphate in a platinum or porcelain crucible at a low temperature. Dissolve the melt in 5 percent sulphuric acid or in hot 5 percent tartaric acid solution, filter, wash and ignite the residue at low temperature and fuse again. Re-extract the melt and combine the extracts, make up the volume in a volumetric flask and take aliquots (*see* **4.3**).

3.3 Biological Materials

3.3.1 *Reagents*

a) *Concentrated sulphuric acid* — *See* IS : 266-1977*.

b) *Dilute nitric acid* — 1:1 (*v/v*).

c) *Perchloric acid* — 70 percent.

d) *Sodium hydroxide solution* — 40 percent.

3.3.2 *Procedure* — Transfer 2 ml blood or 10 ml urine of 2 g of organ to a 500-ml Kjeldahl flask and add a few glass beads. Add 4 ml concentrated sulphuric acid, 5 ml each of dilute nitric acid and 70 percent perchloric acid. Heat gently and, if charring occurs, continue adding small amounts of nitric and perchloric acid in the same proportions until the solution is clear. Heat until all white fumes are expelled from the flask. Cool, dilute with water and make distinctly alkaline to litmus with sodium hydroxide solution. Boil for several minutes and cool. Filter the solution and dilute to 100 ml in a volumetric flask. Take aliquots (*see* **4.3**).

4. METHOD A — USING THIOCYANATE WITH A REDUCING AGENT

4.0 Outline of the Method — Tungsten in mildly alkaline solution or as a complex with tartaric acid forms yellow complex with thiocyanate after acidification and reduction with stannous chloride. The absorbance is measured at 420 nm and tungsten is estimated from calibration curve.

4.1 Reagents

a) *Stannous Chloride Solution* — Dissolve 70 g stannous chloride dihydrate ($SnCl_2.2H_2O$) in 1 litre of concentrated hydrochloric acid. Prepare fresh every week.

b) *Tartaric Acid Solution* — 50 percent.

c) *Sodium Thiocyanate Solution* — 50 percent.

d) *Antimony Pentachloride Solution* — Add saturated potassium bromate solution to a hot antimony trichloride solution containing 0·5 per cent antimony in 4 N hydrochloric acid until the colour of the bromine appears.

e) *Sulphuric Acid Solution* — 6 N.

f) *Bromine*

g) *Stock Tungsten Solution* — Dissove 0·179 4 g of sodium tungstate dihydrate in water and dilute to 1 000 ml. The tungsten concentration of this solution is 0·1 mg/ml.

h) *Standard Tungsten Solution* — Dilute 10 ml of stock solution to 100 ml so that tungsten concentration of the standard solution is 0·01 mg/ml.

4.2 Calibration Curve — Transfer 1, 2, 4, 6, 8 and 10 ml of the standard solution [*see* **4.1** (*h*)] to 25 ml volumetric flask, add 2 ml of 50 percent tartaric acid solution and 1·5 ml of 50 percent sodium thiocyanate solution. Make up the volume with stannous chloride. Read absorbance at 420 nm after 20 minutes against a reagent blank. Plot a calibration curve in terms of mg tungsten in 25 ml of solution versus absorbance.

NOTE — When tartaric acid is used, only sodium thiocyanate has to be used as potassium thiocyanate will precipitate potassium bitartrate.

4.3 Procedure

4.3.1 *Separation of Molybdenum as Sulphide* (if present) — To an aliquot of the sample solution (*see* **3**) in a beaker, add 1 ml of tartaric acid solution, 0·5 ml of 6 N sulphuric acid and 0·2 ml of antimony pentachloride solution. Allow to stand till the solution is clear. Cover the beaker and pass a rapid stream of hydrogen sulphide for 10 minutes. Heat the solution to boiling while continuing the hydrogen sulphide. Remove from heat and pass hydrogen sulphide for another 10 minutes. Stir and let it stand for 2 hours, *Min.* Filter the precipitate on a filter paper No. 40 and wash with a few ml of cold water containing a drop of 6 N sulphuric acid. Evaporate the combined filtrate and washings to 15 ml. Cool and add 5 drops of bromine water until a yellow colour persists for 2 minutes. Add 0·2 ml of the antimony pentachloride solution and precipitate with hydrogen sulphide again. Let it stand overnight and filter the precipitate on No. 40 filter paper. Wash the precipitate with 3 ml of cold water containing a drop of 6 N sulphuric acid. Evaporate combined filtrate and washings to 15 ml in a 50-ml beaker. Cool, transfer to a separating funnel and extract with 5 ml of ether. Wash the ether layer with 2 ml water, add the washings to the bulk solution discarding the ether extracts.

4.3.2 Transfer the solution to a 25-ml volumetric flask and proceed as in **4.2**.

NOTE 1 — With sample solution containing no molybdenum and in the case of silicate materials and geological samples, such as, rocks and soils, the procedure given in **4.3.1** may be omitted and the determination is carried out as in **4.3.2**.

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*Specification for sulphuric acid (*second revision*).

Note 2 — Fluoride and nitrate inhibit colour development and must be completely removed. Phosphate does not interfere.

Note 3 — Tungsten thiocyanate complex can be extracted by solvents to avoid interference by coloured complexes of nickel, chromium, cobalt, vanadium, etc.

4.4 Calculation — Convert the absorbance reading to tungsten from the calibration curve:

$$\text{Tungsten, percent by mass} = \frac{A}{B \times 10}$$

where

A = mass of tungsten from the calibration curve in mg, and

B = mass of sample in g represented in the aliquot used.

5. METHOD B — USING TOLUENE-3, 4-DITHIOL

5.0 Outline of the Method — Tolune-3, 4-dithiol forms a bluish green complex with tungsten (V) and tungsten (VI) which can be extracted with butyl acetate, petroleum ether or other organic solvents and estimated photometrically at 6·25 nm.

5.1 Reagents

a) *Toluene-3, 4-Dithiol Solution* — Dissolve 1 g of toluene-3, 4-dithiol in water containing 5 g of sodium hydroxide and make up the volume to 500 ml in a volumetric flask and store in a refrigerator. Fresh solution shall be prepared every week.

b) *Sulphuric-Citric Acid Solution* — Dissolve 20 g citric monohydrate in 500 ml of 1 : 3 sulphuric acid and dilute to 1 000 ml with the same acid.

c) *Dilute Sulphuric Acid* — 20 N.

d) *Stannous Chloride* — Dissolve 100 g stannous chloride dihydrate and 5 mg cuprous chloride in 400 ml 1 : 1 hydrochloric acid by heating. Cool and dilute to 500 ml with 1 : 1 hydrochloric acid. Add a few pieces of tin and store in a stoppered bottle.

e) *Ferric Sulphate Solution* — Dissolve 5 g ferric sulphate in 100 ml of 1 : 9 sulphuric acid.

f) *Butyl Acetate*

g) *Standard Tungsten Solution* — *see* **4.1** (h).

5.2 Calibration Curve — To each of five 200-ml beakers, add 25 ml of 1 : 3 sulphuric acid. Transfer 1, 2, 3 and 5 ml of standard solution of tungsten to four of the beakers and use the fifth as blank. Add 0·2 ml ferric sulphate solution. Add 50 ml concentrated hydrochloric acid and 5 ml stannous chloride solution. Place the beakers on a steam bath. Heat for 3 minutes. Add 15 ml dithiol solution, mix and heat for 10 minutes. Cool and transfer to 250 ml separating funnels. Add 20 ml butyl acetate with a pipette. Shake for 20 minutes and allow to separate. Transfer the butyl acetate layer to a dry stoppered test tube. Take absorbance readings at 625 nm against blank. Plot absorbance against mg tungsten per 20 ml solution.

5.3 Procedure

5.3.1 *Separation of Molybdenum by Solvent Extraction* — To an aliquot of the sample solution, add 20 ml of sulphuric-citric acid solution and digest to get a clear solution. Add 7·5 ml of 1 : 1 sulphuric acid saturated with sulphur dioxide and 0·2 ml ferric sulphate solution. Add 5 ml of dithiol solution, mix, and allow to stand for 5 minutes in a water bath. Cool and transfer to a separating funnel and add 10 ml chloroform. Shake for 1 minute. Allow to separate and remove the chloroform layer.

5.3.1.1 Repeat extraction with 5 ml chloroform and discard the chloroform layer. Filter the aqueous phase into a beaker and heat in a water bath for 10 minutes. Cool, add 2·5 ml dithiol solution and shake for 10 seconds. Again heat for 5 minutes, cool, transfer to a separating funnel and add 5 ml chloroform and shake for 1 minute. Allow to separate and discard the chloroform layer.

5.3.2 Transfer the aqueous layer to a beaker and heat for 15 minutes in a steam bath.

5.4 Calculation — Convert the absorbance reading to tungsten from calibration curve :

$$\text{Tungsten, percent by mass} = \frac{A}{B \times 10}$$

where

A = mass of tungsten in mg from calibration curve, and

B = mass of sample in g represented in the aliquot used.

Note 1 — Citric acid suppresses tungsten (VI) — dithiol complex formation and not molybdenum — dithiol complex. The molybdenum complex is removed by chloroform extraction. Citric acid does not interfere with tungsten (V) — dithiol complex which is formed after reduction with stannous chloride.

Note 2 — Quantitative extraction of tungsten is obtained either in the presence of phosphoric acid in the solution or when iron, titanium, etc, are present,

BUREAU OF INDIAN STANDARDS

Headquarters:

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